

## CLAIMS

1. A catalyst for addition polymerization of olefinically unsaturated monomers comprising:

5 a) a first compound MY wherein M is a transition metal in a low  
valency state or a transition metal in a low valency state coordinated to at  
least one coordinating non-charged ligand; and Y is a monovalent, divalent  
or polyvalent counterion;

b) an initiator compound comprising a homolytically cleavable  
bond with a halogen atom; and

c) an organodiimine, wherein at least one of the nitrogens of the diimine is not part of an aromatic ring.

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2. A catalyst for addition polymerization of olefinically unsaturated monomers comprising:

d) A first component of Formula

20  $[ML_m]^{n+} A^{n-}$ 

wherein: M = a transition metal of low valency state

L = an organodiimine where at least one of the  
nitrogens of the diimine is not a part of an aromatic ring.

A = an anion

n = an integer of 1 to 3

5

m = an integer of 1 to 2; and

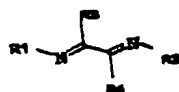
e) an initiator compound comprising a homolytically cleavable bond  
with a halogen atom.

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3.

A catalyst according to any previous claim wherein the organodiimine  
is selected from the group consisting of:

a 1,4-diaza-1,3-butadiene

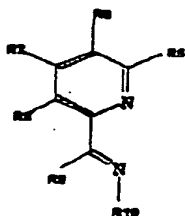


Formula 24

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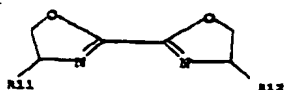
a 2-pyridine carbaldehyde imine

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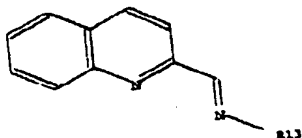
Formula 25

an oxazolidone



Formula 26

or a quinoline carbaldehyde



Formula 27

5 wherein:

$R_1$ ,  $R_2$ ,  $R_{10}$ ,  $R_{11}$ ,  $R_{12}$  and  $R_{13}$  are independently selectable and may be selected from the group consisting of H, straight chain, branched chain or cyclic saturated alkyl, hydroxyalkyl, carboxyalkyl, aryl,  $CH_2$  Ar, wherein Ar is aryl or substituted or a halogen;

10  $R_3$  to  $R_9$  are independently selectable and may be selected from the group consisting of H, straight chain, branched chain or cyclic alkyl, hydroxyalkyl,

carboxyalkyl, aryl,  $\text{CH}_2 \text{ Ar}$ , a halogen,  $\text{OCH}_{2n+1}$ , wherein  $n$  is an integer of 1 to 20,  $\text{NO}_2$ ,  $\text{CN}$ ,

$\text{O} = \text{CR}$ , wherein  $\text{R} = \text{alkyl}$ , aryl, substituted aryl, benzyl  $\text{PhCH}_2$  or a substituted benzyl.

5

<sup>3</sup>  
4. A catalyst according to claim 3 wherein  $\text{R}_1$  to  $\text{R}_{13}$  are selected from the group consisting of  $\text{C}_1$  to  $\text{C}_{20}$  alkyl,  $\text{C}_1$  to  $\text{C}_{20}$  hydroxyalkyl,  $\text{C}_1$  to  $\text{C}_{20}$  carboxyalkyl, n-propylisopropyl, n-butyl, sec-butyl, tert-butyl, cyclohexyl, 2-ethylhexyl, octyldecyl and lauryl.

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<sup>4</sup>  
5. A catalyst according to claim 3 or claim 4, wherein the organodiimine comprises a chiral center.

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<sup>5</sup>  
6. A catalyst according to claims 3 to 5 wherein one or more adjacent  $\text{R}_1$  and  $\text{R}_3$ ,  $\text{R}_3$  and  $\text{R}_4$ ,  $\text{R}_4$  and  $\text{R}_2$ ,  $\text{R}_{10}$  and  $\text{R}_9$ ,  $\text{R}_8$  and  $\text{R}_9$ ,  $\text{R}_8$  and  $\text{R}_7$ ,  $\text{R}_7$  and  $\text{R}_6$ ,  $\text{R}_6$  and  $\text{R}_5$  groups are selected from the group consisting of alkyl, cycloalkenyl, polycycloalkyl, polycycloalkenyl and cyclicaryl, containing 5 to 8 carbon atoms.

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7. <sup>6</sup> A catalyst according to any previous claim wherein M is selected from the group consisting of Cu(I), Fe(II), Co(II), Ru(II), Ni(II) Sm(II), Ag(I) and Yb(II).

5 8. A catalyst according to any of claims 1 and 3 to 7, wherein Y is selected from the group consisting of Cl, Br, I, NO<sub>3</sub>, PF<sub>6</sub>, BF<sub>4</sub>, SO<sub>4</sub> and CF<sub>3</sub> SO<sub>3</sub>, CN, SPh, ScN and SePh.

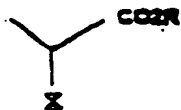
9. A catalyst according to any of claims 2 to 7 wherein A is selected from the group consisting of Cl, Br, F, I, NO<sub>3</sub>, SO<sub>4</sub> and CuX<sub>2</sub>, wherein X is a halogen.

10. A catalyst according to claim 1, wherein the initiator is selected from the group consisting of:

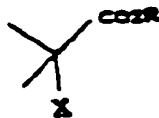
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RX

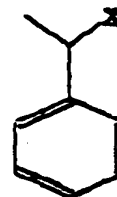
Formula 2,



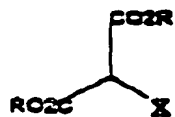
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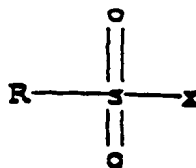
Formula 4,



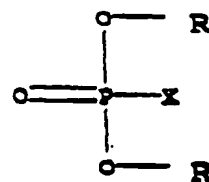
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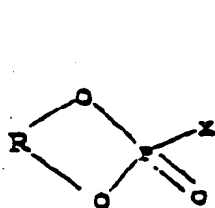
Formula 6,



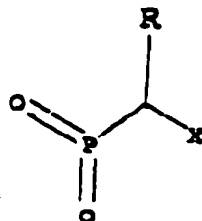
Formula 7,



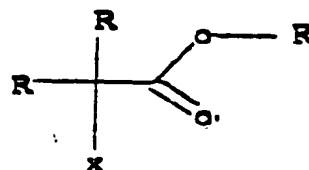
Formula 8,



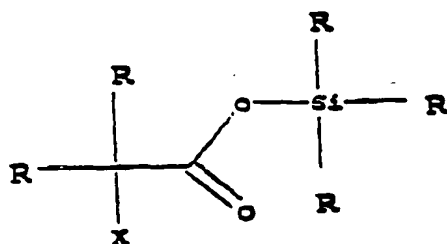
Formula 9,



Formula 10,



Formula 11, and

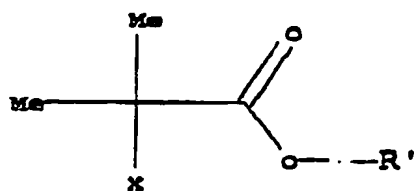


Formula 12,

wherein R is independently selectable and is selected from the group consisting of straight chain alkyl, branched chain alkyl, cyclic alkyl, hydrogen, substituted alkyl, hydroxyalkyl, carboxyalkyl, aryl and substituted aryl and substituted benzyl,

and wherein X = a halide.

11. A catalyst according to claim 10, wherein the initiator is



wherein:

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$X = \text{Br, I or Cl, r}$

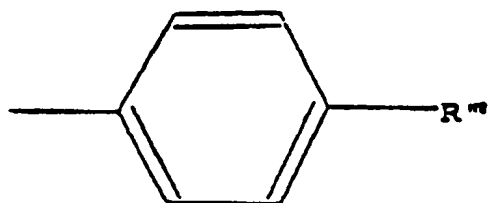
$R' = -\text{H,}$

$-(\text{CH}_2)_p\text{R}''$ , wherein  $p$  is a whole number and  $\text{R}'' = \text{H, OH,}$

$\text{NH}_2, \text{SO}_3\text{H, COOH, halide, COX,}$  where  $X$  is Br, I or Cl,

10

or



15

$\text{R}''' = -\text{COOH, -COX,}$  where  $X$  is Br, I or Cl,  $-\text{OH, -NH}_2$  or  $-\text{SO}_3\text{H}$

12. A catalyst according to claim 11 wherein b is 2-hydroxyethyl-2' bromopropionate.

5           13. A method for addition polymerization of one or more olefinically saturated monomers comprising:  
addition polymerizing one or more olefinically saturated monomers  
using the catalyst of claim 1.

10           14. The method according to claim 13, wherein the addition  
polymerization is conducted at a temperature between -20°C to 200°C.

15           15. The method according to claim 14, wherein the addition  
polymerization is conducted at a temperature between 20°C and 130°C.

20           16. The method according to claim 13, wherein the olefinically saturated monomers are selected from methyl methacrylate, ethyl methacrylate, propyl methacrylate, including all isomers thereof, butyl methacrylate, including all isomers thereof, other alkyl methacrylates, corresponding acrylates, functionalized methacrylates and acrylates,



fluoroalkyl (meth)acrylates, methacrylic acid, acrylic acid, fumaric acid and esters thereof, itaconic acid and esters thereof, nucleic anhydride, styrene,  $\alpha$ -methyl styrene, vinyl halides, acrylonitrile, methacrylonitrile, vinylidene halides of formula  $\text{CH}_2\text{-C(Hal)}_2$  wherein each halogen is independently Cl or F, optionally substituted butadiene of the formula

$\text{CH}_2=\text{C(R}_{15})\text{C(R}_{15})=\text{CH}_2$  wherein  $\text{R}_{15}$  is independently H, Cl to C10

alkyl, Cl or F, sulphonic acids or derivatives thereof of formula

$\text{CH}_2=\text{CHSO}_2\text{OM}$  wherein M is NaS, K, Li,  $\text{N(R}_{16})_4$ , or  $-(\text{CH}_2)_2\text{-D}$  wherein

each  $\text{R}_{16}$  is independently H or Cl or C10 alkyl, D is  $\text{CO}_2\text{Z}$ , OH,  $\text{N(R}_{16})_2$

or  $\text{SO}_2\text{OZ}$  and Z is H, Li, Na, K or  $\text{N(R}_{16})_4$ , acrylamide or derivatives

thereof of formula  $\text{CH}_2\text{-C(CH}_3\text{)CON(R}_{16})_2$ , and wherein mixtures thereof.

17. The use of a catalyst, as defined in claims 1 and 3 to 12, according to claims 13 to 16, wherein the ratio (c):(a) is 0.01 to 1000 and the ratio of (a):(b) is 0.0001 to 1000.

18. The use of a catalyst as defined in claims 2 to 12 according to claims 13 to 16 wherein the ratio of M:initiator is between 3:1 and 1:100.

19. The method according to claim 13, wherein the polymerization is conducted in water, a protic solvent or a nonprotic solvent.

20. A method for producing a statistical copolymer, a block polymer,  
a telechelic polymer or a comb and graft copolymer of monomers, the  
5 method comprising:

producing at least one of a statistical copolymer, a block polymer, a  
telechelic polymer and a comb and graft copolymer of monomers using the  
catalyst of claim 1.

21. A catalyst for addition polymerization of olefinically unsaturated  
10 monomers comprising:

(a) a first component of formula  $(ML_m)^{n+}A^{n-}$  wherein

M = a transition metal of low valency state;

L = an organodiimine where at least one of the nitrogens of the  
diimine is not part of an aromatic ring;

15 A = an anion;

n = an integer from 1 to 3;

m = an integer from 1 to 2; and

(b) an initiator compound comprising a homolytically cleavable  
bond with a halogen atom.--

22. A catalyst according to claim 21, wherein A is selected from the group consisting of Cl, Br, F, I, NO<sub>3</sub>, SO<sub>4</sub> and CuX<sub>2</sub>, wherein X is a halogen.